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Note

Analysis of thermal expansivity of NaCl and KCl crystals at high temperatures

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Abstract In the present study, various relationships for temperature dependence of thermal expansivity in high temperature domain at 1 bar pressure are deduced for NaCl and KCl crystals. These relationships are derived on the basis of temperature dependence of volume expansion ratio studied recently. It is found that among the various relationships, the thermal expansivity derived from the Srivastava equation of volume expansion ratio shows close agreement with the experimental data available in literature. The present relationship for thermal expansivity may be used to understand the high temperature behaviour of solids.

Keywords Volume expansion ratio, thermal expansivity

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Thermal expansivity is a very important parametric quantity for understanding the thermodynamic and thermoelastic behaviour of solids at high temperatures because it has been emphasized [1] that most of the serious errors in the calculations of thermodynamic functions arise due to uncertainty of thermal expansivity at high temperatures. In the present communication, the thermal expansivity for NaCl and KCl is analyzed in high temperature region with the help of different models predicting temperature dependence of volume expansion ratio.

It has been found [2] that thermal expansivity goes on increasing in the high temperature region. Anderson *et al* [3] have found that the variation of α with temperature T is linear and can be represented by the following relationship

$$\alpha = \alpha_0 \left[1 - \alpha_0 \delta_T^0 (T - T_0)\right]^{-1}, \tag{1}$$

where α_0 and δ_T^0 are the values of thermal expansivity and the Anderson-Gruneisen parameter at initial temperature T_0, which may be taken equal to 300K for solids under consideration, because eq.(1) is valid only at temperatures higher than θ_D. Now, using the following mathematical definition of thermal expansivity

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{2}$$

alongwith eq.(1), we get the expression for temperature dependence of volume expansion ratio as

$$\frac{V}{V_0} = \left[1 - \alpha_0 \delta_T^0 (T - T_0)\right]^{-1/\delta_T^0}, \tag{3}$$

where V_0 is the volume V at initial temperature $T_0 = 300$K.

Expression for volume expansion ratio used by Vijay and Verma [4] can be written as follows :

$$\frac{V}{V_0} = 1 + \frac{1 - \left[1 - (2/K_0)(K_0' + 1)\Delta P_{TH}\right]^{1/2}}{K_0' + 1} \tag{4}$$

where K_0 and K_0' are the values of isothermal bulk modulus (K_T) and its first pressure derivative (dK_T/dP) at $P = 0$. The parameter ΔP_{TH} is known as thermal pressure and according to the Anderson [2] it can be expressed as

$$\Delta P_{TH} = \alpha K_T (T - T_0), \tag{5}$$

where α and K_T are taken corresponding to the Debye temperature, which can be expressed as α_0 and K_0 for solids under study. Thus, eq. (5) can be replaced as eq.

$$\Delta P_{III} = \alpha_0 K_0 (T - T_0) . \tag{6}$$

The method of calculating (V/V_0) in the form of eq. (4) is originally discovered by Shanker *et al* [5]. The Shanker equation (4) has been found to be valid for a number of solids studied recently [6-12]. The Shanker equation has been derived from Taylor series expansion of the potential energy including the higher order terms in the formulation originally due to Born and Huang [5,13,14]. Now, combination of eqs. (4) and (6) results in

$$\frac{V}{V_0} = C - \frac{1}{(K_0' + 1)}\left[1 - 2\alpha_0 (K_0' + 1)(T - T_0)\right]^{1/2}, \tag{7}$$

where $C = (K_0' + 2)/(K_0' + 1) =$ constant. Differentiating eq. (7) with respect to temperature T at $P = 0$ and with the help of eq. (2), we get following expression for temperature dependence of thermal expansivity

$$\alpha = \alpha_0 (V/V_0)^{-1}\left[1 - 2\alpha_0 (K_0' + 1)(T - T_0)\right]^{-1/2}. \tag{8}$$

Since α_0 is in order of $10^{-5} K^{-1}$, therefore, ignoring higher order terms in the expansion of right hand side of eq. (8), we obtain

$$\alpha = \alpha_0 (V/V_0)^{-1}\left[1 + \alpha_0 (K_0' + 1)(T - T_0)\right]. \tag{9}$$

Fang [15] obtained following relationship for predicting volume thermal expansion of alkali halides at high temperatures

$$(V/V_0) = 1 - \frac{1}{\delta_T^0}\ln\left[1 - \alpha_0 \delta_T^0 (T - T_0)\right]. \tag{10}$$

Eq. (10) is derived by the following differential equation [15]

$$(dV/dT) = C_0/K_T, \tag{11}$$

where $C_0 = \alpha_0 K_0 V_0$ and (12)

$$K_T = K_0\left[1 - \alpha_0 \delta_T^0 (T - T_0)\right]. \tag{13}$$

Fang [15] assumed that two different diffusional deriving force models presented both by Sharma and Sharma [16] and Singh [17] are equivalent. Eq. (11) yields following expression for temperature dependence of thermal expansivity

$$\alpha = \alpha_0 (V/V_0)^{-1}\left[1 - \alpha_0 \delta_T^0 (T - T_0)\right]^{-1}. \tag{14}$$

Srivastava [18] obtained an expression for temperature dependence of volume expansion ratio, which can be written as (for solids under consideration)

$$(V/V_0) = 1 + (\alpha_0/m)\left[\exp m(T - T_0) - 1\right], \tag{15}$$

where m is a material dependent constant. The above relationship is based on the fact that a systematic linear relationship is observed between $\ln(\alpha V/\alpha_0 V_0)$ and $(T - T_0)$ for NaCl and KCl, which results in the following expression for thermal expansivity

$$\alpha = \alpha_0 (V/V_0)^{-1} \exp m(T - T_0) . \tag{16}$$

Ignoring higher order terms in the expansion of right hand side of eq. (16)

$$\alpha = \alpha_0 (V/V_0)^{-1}\left[1 + m(T - T_0)\right]. \tag{17}$$

Combination of eq. (15) and eq. (17) yields

$$\alpha = \alpha_0\left[1 + m(T - T_0)\right] \times \left[1 + \alpha_0 (T - T_0)\right]^{-1}. \tag{18}$$

Here, the term $\left[\exp m(T - T_0) - 1\right]$ in the expression of (V/V_0) is written as $m(T - T_0)$ because of ignorance of higher order terms. Eq. (18) can also be written as

$$\alpha = \alpha_0\left[1 + m(T - T_0)\right] \times \left[1 - \alpha_0 (T - T_0)\right]. \tag{19}$$

Now, the temperature dependence of volume expansion ratio for NaCl and KCl are calculated through eqs. (3), (4), (10) and (15). Values of α_0, K_0, δ_T^0 and K_0' are taken as 11.8×10^{-5} K^{-1}, 24 GPa, 5.56 and 5.38 respectively, in calculations for NaCl, while for KCl, these values are selected as $11 \times 10^{-5} K^{-1}$, 17GPa, 5.84 and 5.46, respectively. Such values are based on the experimental data tabulated by Anderson [2]. The value of m obtained with the slope of the plots between $\ln(\alpha V/\alpha_0 V_0)$ and $(T - T_0)$, are found as $9 \times 10^{-4} K^{-1}$ and $8.6 \times 10^{-4} K^{-1}$, respectively for NaCl and KCl. It is necessary to mention here that Fang[15] used the values of δ_T^0 as 5.95 and 6.29 for NaCl

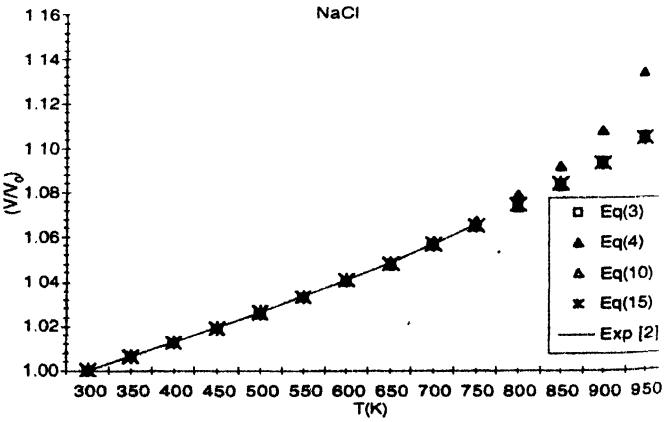

Figure 1. Comparison of predicted values of volume expansion ratio, through various equations, with the experiment.

and KCl, respectively, available then in the literature[19]. Therefore, such values are used here to compute the values of volume expansion ratio with the help of eq.(10). Predicted values of temperature dependence of volume expansion ratio for solids under consideration are compared with experiment [2] in Figures 1 and 2. It is found by Srivastava[18] that the eq. (15) shows good agreement with the experimental data for both solids. Eq. [10] of Fang [15] gives close agreement with the experimental data for KCl while for NaCl, the results deviate from the experiment. This deviation becomes significant as temperature rises. Thus, the present analysis reflects the superiority of Srivastava model [18] over other models proposed by Anderson *et al* [3], Shanker *et al* [5] and Fang [15].

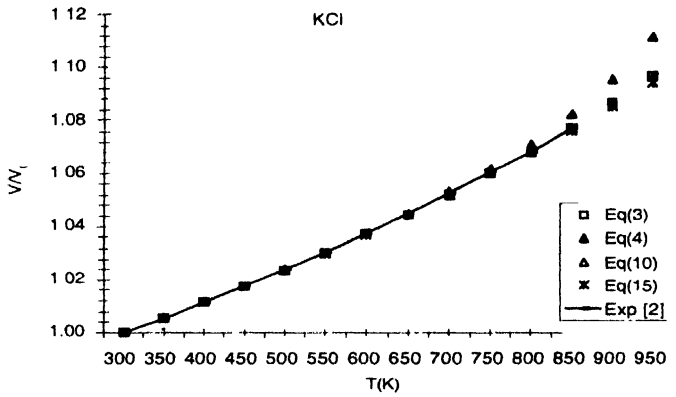

Figure 2. Comparison of predicted values of volume expansion ratio, through various equations, with the experiment.

Thermal expansivity in high temperature domain for solids under consideration are predicted by eqs. (1),(8), (9), (14), (16) and (19).Results are compared in Figures 3 and 4. It is found by Srivastava[18] that eq. (16) shows very close agreement with the experimental data. Further, the predicted values of thermal expansivity (eq.(19)) obtained by Srivastava[18] deviates

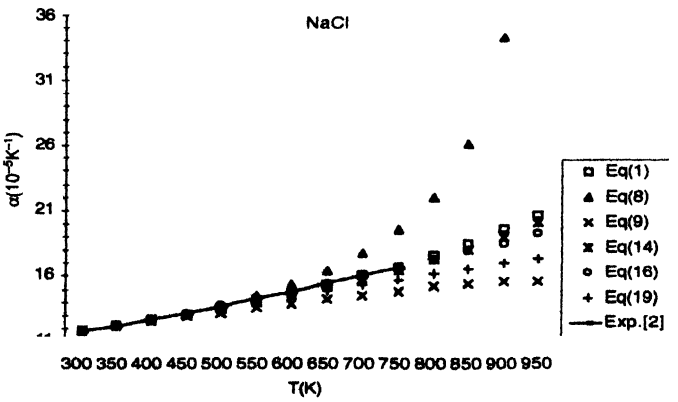

Figure 3. Comparison of predicted values of thermal expansivity, through various equations, with the experiment.

significantly from the experimental data at very high temperature, which indicates that the ignorance of higher order terms in the derivation of eq. (19) is not acceptable. It is also found that thermal expansivity calculated by Shanker *et al* [5] deviates significantly in very high temperature domain. It is interesting to compare Anderson eq. (1) of Anderson [2] with eq. (14) of Fang [15], Both equations are identical, however, an extra term $(V/V_0)^{-1}$ emerges in eq. (14) of Fang. Thus, both equations show identical results because the term $(V/V_0)^{-1}$ is significant only in very high temperature region.

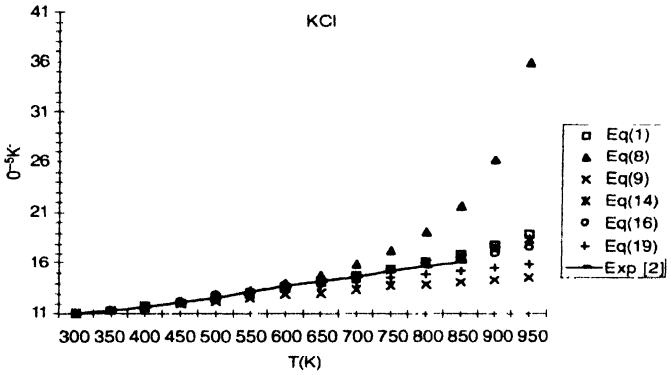

Figure 4. Comparison of predicted values of thermal expansivity, through various equations, with the experiment

Thus, it may be concluded that among the various relationships derived here for temperature dependence of thermal expansivity, the eq. (16) of Srivastava shows better agreement with the experimental data [2] for alkali halides under consideration. Eq. (16) also reflects that thermal expansivity is a complex function of temperature because of the exponential term along with a term $(V/V_0)^{-1}$, which is also temperature dependent. Eq. (16) of Srivastava may be used to understand the thermodynamic behaviour of solids because it is not only restricted for NaCl and KCl [18].

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